



TITLE:

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CITATION:

Nakahara, Masaru ...[et al]. Ionic solutions under high pressures V : pressure effects on the walden products and hydration of Et₄N⁺ and ClO₄⁻ ions in water. The Review of Physical Chemistry of Japan 1974, 43(2): 71-81

ISSUE DATE:

1974-01-31

URL:

<http://hdl.handle.net/2433/46989>

RIGHT:

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 43, NO. 2, 1973

IONIC SOLUTIONS UNDER HIGH PRESSURES V

Pressure Effects on the Walden Products and Hydration of
 Et_4N^+ and ClO_4^- Ions in Water

BY MASARU NAKAHARA AND JIRO OSUGI

The electrical conductivities of aqueous solutions at high pressures up to 5,000 atm have been measured in the concentration range from 10^{-4} to 10^{-3}N for tetraethylammonium chloride, Et_4NCl at 25 and 40°C and for tetraethylammonium perchlorate, Et_4NClO_4 at 25°C. The equivalent conductances of the electrolytes at infinite dilution have been determined by means of the Onsager equation which was verified to be valid in the dilute solutions at high pressures in the previous papers^{1,2}. The limiting equivalent conductances determined at high pressures were separated into the single-ion ones on the basis of the same assumption as used in the previous paper³. Although the limiting equivalent conductance of Et_4N^+ has a maximum against pressure at 25°C like other tetraalkylammonium ions, that of ClO_4^- , surprisingly and exceptionally, has no maximum even at 25°C where the viscosity of solvent water has a minimum at about 650 atm³. The Walden product of Et_4N^+ decreases slightly with increasing pressure at 25°C and, probably, so at 40°C like that of Me_4N^+ . On the other hand, the Walden product of ClO_4^- at 25°C dramatically decreases with increasing pressure. Thus, it is considered that the pressure dependence of the limiting equivalent conductance of the ion in water can not be explained merely in terms of such bulk properties of water as the viscosity and dielectric constant. These differences in the pressure coefficients of the Walden products were ascribed to the differences between the density of the hydration shell and that of the bulk water.

Introduction

Colladon and Sturm⁴) are the first persons to attempt to examine the effect of pressure on the electrical conductivities of electrolyte solutions, when it was not yet known what carries electricity in solution. In 1885, first of all, Fink⁵) established that pressure (up to 500 atm) does decrease the electrical resistances of electrolyte solutions; it was two years before the appearance of the Arrhenius

(Received September 10, 1973)

1) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)

2) M. Nakahara, *ibid.*, **42**, 75 (1972)

3) J. B. Cappi, Ph. D. Thesis, London University (1964)

4) D. Colladon and C. Sturm, *Ann. Chim. Phys.*, **36**, 231 (1827)

5) J. Fink, *Wied. Ann.*, **26**, 481 (1885)

theory for the behavior of electrolyte solutions. In the 1890's, Röntgen⁶⁾, Fanjung⁷⁾ and Tammann⁸⁾ first found a parallelism between the pressure dependence of the electrical conductivities of aqueous solutions and that of the solvent fluidity measured by Cohen⁹⁾. Strictly speaking, however, those early works were not so much accurate but only phenomenological, even after the eminent Debye-Hückel theory¹⁰⁾ for the strong electrolyte solution was developed in 1923. It seems to the authors that first great efforts to determine accurately the limiting equivalent conductances at high pressures were made in the 1950's by Hamann and his coworkers in particular for the purpose of examining the pressure effect on the ionization of weak electrolytes. In the 1960's, the accurately determined limiting equivalent conductances at high pressures began to be analyzed in terms of the transition state theory¹³⁾ by Brummer and Hills^{14,15)}, Osugi, Shimizu and Takizawa¹⁶⁾, and Adams and Laidler¹⁷⁾, and also in terms of the dielectric relaxation effect by Skinner and Fuoss¹⁸⁾ and Cussler and Fuoss¹⁹⁾.

When we deal with a transport property in solution, there is one fundamental question as to how much the transport property might reflect the equilibrium property of ions in solution. In the case of ionic conductance, however, there would be fairly good correspondence between them for the following reasons. The ions in solution are originally moving very rapidly in a random way colliding with the solvent molecules or with each other, as well-known as Brownian motion. When an external electric field is applied to the system, the ions begin to move preferentially in the direction of the applied field. At this time, if the external perturbation is so weak, as often in the conductance measurement, that it may not disturb the internal field exerted by the ions themselves and polar solvent molecules, the limiting ionic equivalent conductance would minutely reflect the ion-solvent interaction in the equilibrium state. In consequence, the limiting ionic equivalent conductance could be used as a useful probe to study ionic hydration. As a matter of fact, it was previously reported²⁰⁾ that there are linear correlations between the hydration number calculated from the limiting ionic equivalent conductance and the hydration enthalpy for the alkali metal ions and for the halogen ions at normal pressure.

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- 6) W. C. Röntgen, *Nachrichten der k. Gesellsch. zu Göttingen*, 509 (1893)
 - 7) I. Fanjung, *Z. Phys. Chem.*, **14**, 673 (1894)
 - 8) G. Tammann, *ibid.*, **17**, 725 (1895)
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 - 16) J. Osugi, K. Shimizu and H. Takizawa, *This Journal*, **34**, 55 (1964)
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 - 18) J. K. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **71**, 4455 (1967)
 - 19) E. L. Cussler and R. M. Fuoss, *ibid.*, **71**, 4459 (1967)
 - 20) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sec.)*, **92**, 785 (1971)

Experimental

Tetraethylammonium chloride, Et_4NCl was obtained by using anion exchange resin from its bromide which was first synthesized by the Menshutkin reaction. Et_4NCl salt was three times recrystallized from its methanol solution by adding chilled ether, and dried in vacuum at about 50°C for a week. Tetraethylammonium perchlorate was precipitated by adding excess amount of perchloric acid to the aqueous solution of Et_4NBr^* , recrystallized twice from its aqueous solution, and dried in vacuum at room temperature for 3 days after heated up to 100°C for 2 hours with great care to avoid explosion. The dilute sample solutions were prepared from stock solutions just in the same way as before^{1, 21)}.

The high-pressure apparatus and the conductivity cell were already described elsewhere.

Results and Discussion

Determination of $\Lambda^{\circ(P)}$

The equivalent conductances, $\Lambda^{(P)}$ of Et_4NCl and Et_4NClO_4 in dilute aqueous solution at pressure P were determined, after the corrections for the solvent conductivity and changes in concentration and cell constant with pressure had been made just in the same manner as the previous study¹⁾. Then, the equivalent conductances at infinite dilution at pressure P , $\Lambda^{\circ(P)}$ were obtained with the aid of Onsager's equation for conductance,

$$\Lambda = \Lambda^{\circ} - (\alpha\Lambda^{\circ} + \beta)\sqrt{C}; \quad (1)$$

that is,

$$\Lambda^{\circ} = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}}, \quad (2)$$

from which $\Lambda^{\circ(P)}$ of Et_4NCl at 25 and 40°C and Et_4NClO_4 at 25°C were calculated and given in Tables 1~3. The adequacy of this method to obtain $\Lambda^{\circ(P)}$ from $\Lambda^{(P)}$ in the dilute concentration range would be supported by the approximate constancy of $\Lambda^{\circ(P)}$ around their mean value within the experimental error, which was already found in the previous study on Me_4NCl and Bu_4NCl ²⁾. However, it was reported^{22, 23)} that the direct graphical extrapolation of the conductance data of Et_4NCl to infinite dilution with the aid of the theoretical limiting slope was not satisfactory exceptionally. When the conductances of Et_4NCl shown in Table 1 are compared with those measured at a higher concentration by Horne and Young²⁴⁾, there are rather large discrepancies between them as found

* This salt was kindly supplied by Mr. T. Hori, Laboratory of Analytical Chemistry of our Department.

21) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)

22) A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 1763 (1968)

23) S. B. Brummer and A. B. Gancy, "Water and Aqueous Solutions", Chap. 19, Part I, ed. by R. A. Horne, Wiley-Interscience, New York (1972)

24) R. A. Horne and R. P. Young, *J. Phys. Chem.*, **72**, 1763 (1968)

in the cases of Me_4NCl and Bu_4NCl ²⁵⁾.

Table 1 $\Lambda^{(P)}$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of Et_4NCl in H_2O at 25°C

Sample* Pressure, atm	A	B	C	D	Average
1	108.9	108.9	108.8	108.8	108.9
500	110.9	110.6	110.7	110.8	110.8
1,000	111.4	111.1	111.4	111.1	111.3
1,500	111.2	110.6	110.9	110.2	110.7
2,000	109.9	109.3	109.7	109.1	109.5
2,500	108.3	107.6	107.8	107.1	107.7
3,000	106.2	105.3	105.7	105.1	105.6
3,500	103.3	102.9	103.1	102.8	103.0
4,000	100.8	100.3	100.3	100.1	100.4
4,500	98.3	97.6	97.7	97.5	97.8
5,000	95.6	95.0	94.9	94.6	95.0

* A: 3.866×10^{-4} N, B: 6.201×10^{-4} N, C: 8.536×10^{-4} N, D: 11.598×10^{-4} N at 1 atm

Table 2 $\Lambda^{(P)}$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of Et_4NCl in H_2O at 40°C

Sample* Pressure, atm	A	B	C	D	Average
1	143.9	143.9	143.8	143.9	143.9
500	143.6	143.7	143.7	143.6	143.7
1,000	142.6	142.6	142.6	142.5	142.6
1,500	141.2	141.2	141.0	141.1	141.1
2,000	139.6	139.1	138.9	139.2	139.2
2,500	137.2	136.5	136.4	136.6	136.6
3,000	134.6	133.8	133.5	133.7	133.9
3,500	131.4	130.5	130.3	130.4	130.7
4,000	128.2	127.2	126.9	127.0	127.3
4,500	124.9	123.6	123.4	123.4	123.8
5,000	121.5	120.1	119.9	119.8	120.4

* A: 3.847×10^{-4} N, B: 5.992×10^{-4} N, C: 8.495×10^{-4} N, D: 11.542×10^{-4} N at 1 atm

Obtaining of $\lambda^{(P)}$ from $\Lambda^{(P)}$

The single-ion equivalent conductances at pressure P , $\lambda^{(P)}$ were calculated on the basis of the same postulate used in Ref. (2); it was assumed that the Walden product of Bu_4N^+ is approximately independent of pressure. In the present calculation, the previous²⁵⁾ interpolations of the values of water viscosity measured by Cappi³⁾ have been corrected as shown in Table 4, because the interpolation from the direct plot of water viscosity, η^* against pressure was found to be less accurate than

25) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)

Table 3 $\lambda^{(P)}$ (ohm⁻¹·cm²·equiv⁻¹) of Et₄NClO₄ in H₂O at 25°C

Sample*	A	B	C	D	Average
Pressure, atm					
1	99.86	99.95	99.82	99.95	99.9
500	98.37	98.71	98.61	98.89	98.6
1,000	95.94	96.49	96.27	96.43	96.3
1,500	93.55	93.82	93.41	93.60	93.6
2,000	90.45	90.69	90.41	90.53	90.5
2,500	87.34	87.46	87.20	87.46	87.4
3,000	84.40	84.38	84.11	84.16	84.3
3,500	81.11	81.11	80.90	80.94	81.0
4,000	77.89	78.02	77.85	77.88	77.9
4,500	74.80	74.99	74.82	74.88	74.9
5,000	71.93	72.08	71.96	72.02	72.0

* A: 4.547×10^{-4} N, B: 7.276×10^{-4} N, C: 9.093×10^{-4} N, D: 10.919×10^{-4} N

that from the plot of $\log \eta^\circ$ against pressure at the high pressures due to the steep dependency of η° upon pressure and the scarcity of the measured points (The corrected values of η° in Table 4 does not make the curve of $\lambda^{(P)}(\text{KCl}) \cdot \eta^\circ$ vs. pressure at 25°C cross that at 40°C; see Fig. 4 in Ref. (1)) The obtained values of $\lambda^{(P)}$ at 25°C are summarized in Table 5, where the values of $\lambda^{(P)}$ of other ions so far investigated are also given for comparison after the above correction has been made. In Table 5, it is seen that the correction does not cause so large alteration in the values of $\lambda^{(P)}$ and the discussion and conclusion in the previous paper might not be amended.

Table 4 The viscosity of water, $\eta^*(\text{cP})$ at 25°C (interpolated by plotting Cappi's data against pressure)

Pressure, atm	Present	Previous ²⁵⁾
1	0.8937	
500	0.8865	
1,000	0.8905	
1,500	0.9053	
2,000	0.9260	0.9266
2,500	0.9532	0.9534
3,000	0.9853	0.9709
3,500	1.0135	1.0022
4,000	1.0589	1.0392
4,500	1.0895	1.0756
5,000	1.1457	1.1163

Table 5 $\lambda^{\circ(P)}$ ($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}$) of the ions in H_2O at 25°C

Ions Pressure, atm	Bu_4N^+	Bu_4N^{+*}	Et_4N^+	Me_4N^+	K^+	Cl^-	ClO_4^-
1	19.4	19.4	32.5	44.7	73.5	76.4	67.4
500	19.6	19.6	32.9	45.0	74.7	77.9	65.7
1,000	19.5	19.5	32.5	44.4	74.6	78.8	63.8
1,500	19.2	19.2	31.8	43.8	74.0	78.9	61.8
2,000	18.7	18.7	30.9	42.8	73.0	78.6	59.6
2,500	18.2	18.2	30.0	41.6	71.9	77.7	57.4
3,000	17.6	17.9	29.0	40.3	70.1	76.6	55.3
3,500	17.1	17.3	27.8	38.9	68.4	75.2	53.2
4,000	16.4	16.7	26.8	37.6	66.6	73.6	51.1
4,500	15.9	16.1	26.0	36.1	64.9	71.8	48.9
5,000	15.1	15.5	24.8	34.5	62.4	70.2	47.2

* From Ref. (2)

The postulate introduced to obtain the single-ion equivalent conductances at infinite dilution at high pressures has been justified in Ref. (2) by comparing the calculated transference numbers of K^+ in KCl ,

$$t^{\circ(P)}(\text{K}^+) = \frac{\lambda^{\circ(P)}(\text{K}^+)}{\Lambda^{\circ(P)}(\text{KCl})} \quad (3)$$

with those directly measured up to 2,000 atm at 25°C . In order to estimate the values of $\lambda^{\circ(P)}$ at 40°C , it was additionally assumed that

$$\frac{t^{\circ(P)}(\text{K}^+)}{t^{\circ(1)}(\text{K}^+)} = \frac{\lambda^{\circ(P)}(\text{K}^+)}{\lambda^{\circ(1)}(\text{K}^+)} \quad (4)$$

Table 6 Walden products of the ions in H_2O at 40°C
($\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{equiv}^{-1}\cdot\text{cP}$)

Ions Pressure, atm	Et_4N^+	Me_4N^+	K^+	Cl^-
1	28.5	41.1	63.0	66.0
500	27.4	39.8	63.7	67.9
1,000	27.9	40.2	64.4	68.5
1,500	27.8	40.9	65.4	70.3
2,000	27.5	39.8	66.2	72.0
2,500	27.5	39.8	67.1	73.2
3,000	27.5	39.8	67.9	74.3
3,500	27.5	39.8	68.7	75.5
4,000	27.2	39.5	69.4	76.8
4,500	27.2	39.5	70.0	77.5
5,000	27.0	39.1	70.3	79.0

is nearly independent of temperature, because in our laboratory²⁶⁾ it has been recently shown that $\tau^{\circ(P)}(\text{K}^+)$ decreases by only 0.7% with the increase in temperature from 15 to 25°C or from 25 to 40°C both at 1,000 and at 1,500 atm. By using the values of $\tau^{\circ(P)}$ at 25°C calculated from the ionic equivalent conductance values in Table 5, $\lambda^{\circ(P)}(\text{Et}_4\text{NCl})$ in Table 2, $\lambda^{\circ(P)}(\text{KCl})$ in Ref. (1), $\lambda^{\circ(P)}(\text{Me}_4\text{NCl})$ in Ref. (2) and $t^{\circ(1)}(\text{K}^+)$ at 40°C in Ref. (27), the single-ion values of the limiting equivalent conductances at 40°C at high pressures were obtained and used for the calculation of the Walden Products in Table 6.

Pressure dependence of $\lambda^{\circ(P)}$

The relative variation of the limiting equivalent conductances of the ions with pressure is shown in Fig. 1. It is to be noted that the pressure dependence of $\lambda^{\circ(P)}$ of tetraalkylammonium ions such as Bu_4N^+ , Et_4N^+ and Me_4N^+ are somewhat similar to each other and, moreover, to that of the viscosity of solvent water. On the other hand, the pressure dependence of $\lambda^{\circ(P)}$ of K^+ , Cl^- and, above all, ClO_4^- are quite different with each other. Furthermore, it is surprising that ClO_4^- ion has no maximum conductance against pressure at 25°C, although all other ions so far studied have a maximum conductance against pressure at the same temperature. These facts would suggest that the limiting ionic equivalent conductance at high pressure can not be interpreted only by such a macroscopic property of the solvent as viscosity, in spite of the early finding and statement by Röntgen, Fanjung and Tamman.

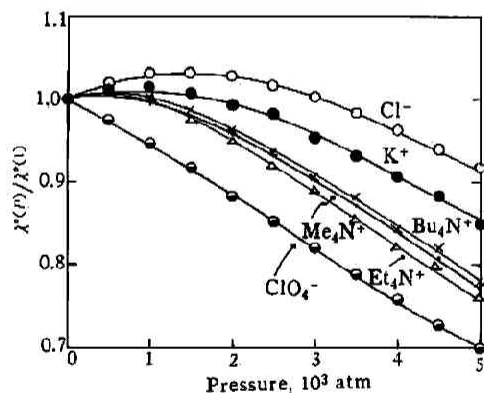


Fig. 1 $\lambda^{\circ(P)}/\lambda^{\circ(1)}$ vs. pressure at 25°C

Variation of the Walden product with pressure

In order to deduct the pressure influence on the macroscopic viscosity of water from that on the ionic conductance, the Walden products, $W = \lambda^{\circ(P)} \cdot \eta^{\circ(P)}$ of the ions at 25°C are calculated by using the values of $\lambda^{\circ(P)}$ in Table 5 and $\eta^{\circ(P)}$ in Table 4 and given in Table 7, and their relative variations with pressure are shown in Fig. 2. There, we see that the pressure coefficient of the Walden product, $\partial W/\partial P$ at 1 atm and 25°C is positive, slightly negative and remarkably negative for Cl^- and K^+ ions,

26) Y. Matsubara, K. Shimizu and J. Osugi, *This Journal*, **43**, 24 (1973)

27) R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940)

Table 7 Walden products of the ions in H₂O at 25°C
(ohm⁻¹·cm²·equiv⁻¹·°C⁻¹)

Ions Pressure, atm	Et ₄ N ⁺	Me ₄ N ⁺	K ⁺	Cl ⁻	ClO ₄ ⁻
1	29.0	39.9	65.7	6.83	60.2
500	29.2	39.9	66.2	69.1	58.2
1,000	28.9	39.5	66.4	70.2	56.8
1,500	28.8	39.7	67.0	71.4	55.9
2,000	28.6	39.7	67.6	72.8	55.2
2,500	28.6	39.7	68.5	74.1	54.7
3,000	28.6	39.7	69.1	75.5	54.5
3,500	28.2	39.4	69.3	76.2	53.9
4,000	28.4	39.8	70.5	77.9	54.1
4,500	28.3	39.3	70.7	78.2	53.3
5,000	28.4	39.5	71.5	80.4	54.1

tetraalkylammonium ions and ClO₄⁻ ion, respectively. Comparing Fig. 2 with Fig. 3^{28,29}, we notice that $\partial W/\partial P$ at 25°C and 1 atm does not correlate with $\partial W/\partial T$ at 1 atm 25°C for these ions. The possible view-points for the interpretation of the pressure and temperature coefficients of the ionic Walden product are summarized in Table 8, where all the view-points but the first one are relevant

Table 8 Prediction of the sign of $\partial W/\partial P$

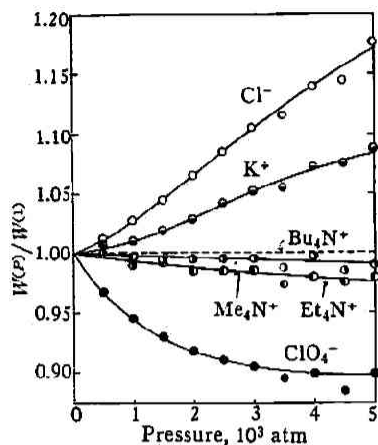
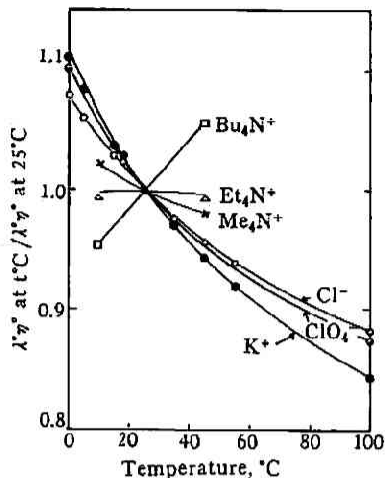
Point of view	Ref.	Sign of $\partial W/\partial P$
C) Compression effect	20, 21	+
D) Dielectric friction theory	18, 19	+
E) Electrostriction theory		-
P) Pressure-induced dehydration	30	+
S) Structural change of water	28	-, 0, +

to ion-solvent interaction at any rate. Before we correlate the pressure coefficient of the ionic Walden product with the ion-solvent interaction, we now consider the theoretical background of W or λ° . Although in very dilute electrolyte solutions, λ has been successfully represented in some quantitative forms by Onsager, Fuoss and others, no satisfactory theory for ionic conductance has been established at the two extremes, at infinite dilution and at high concentration. Owing to this undeveloped stage of the theory for λ° , we could not make any completely quantitative explanation of the pressure

28) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966)

29) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London (1957)

30) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)

Fig. 2 $W(P)/W(1)$ vs. pressure at 25°CFig. 3 Variation of the Walden products with temperature at 1 atm
 λ^* of Bu_4N^+ , Et_4N^+ and Me_4N^+ are cited from Ref. (28), and λ^* of K^+ , Cl^- and ClO_4^- from Ref. (29).

coefficient of the ionic Walden product as yet. Then, we want to try some qualitative discussion by using the modified^{20,21)} Stokes equation,

$$\lambda^* = \frac{|z|eF}{C\eta^*r_e}, \quad (5)$$

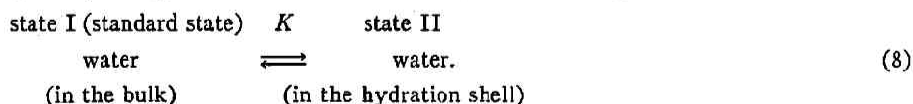
where z , e , F , C , λ^* and r_e are the ionic valence, protonic charge, Faraday constant, hydrodynamic parameter being a function of r_e , solvent viscosity and effective radius of a hydrated ion, respectively. From Eq. (5) we have

$$W = \lambda^*\eta^* = \frac{|z|eF}{Cr_e}. \quad (6)$$

When Eq. (6) is differentiated with respect to pressure, it follows that

$$\frac{\partial W}{\partial P} = -W \frac{\partial r_e}{\partial P} \left(\frac{1}{r_e} + \frac{1}{C} \frac{\partial C}{\partial r_e} \right), \quad (7)$$

where the third factor in the right-hand side has a positive value because $\partial C/\partial r_e$ is positive^{20,21)}. Then, it may be approximated that water exists in the following two states,



For the above equilibrium, we can write

$$K = \frac{a_{\text{II}}}{a_{\text{I}}} \doteq h m \gamma_{\text{II}} \quad (a_{\text{I}} = 1, m \ll 1), \quad (9)$$

where K is the equilibrium constant, a the activity of water, h the hydration number of an ion at infinite dilution, m the concentration of the ion which is arbitrarily very small, and γ_{II} the activity

coefficient of water in the state II. More than ten years ago, the kinetic aspect of the hydration of ions was discussed by Samoilov^{31,32} especially from the view-point of energetics. Now, we attempt to discuss the hydration equilibrium in terms of density. By differentiating the logarithmic form of Eq. (9) with respect to pressure, neglecting the pressure coefficient of τ_{II} and considering the basic thermodynamic relationship, we have

$$\frac{\partial \ln h}{\partial P} = \frac{1}{h} \frac{\partial h}{\partial P} = - \frac{\bar{V}^{\circ}_{II} - \bar{V}^{\circ}_I}{RT}, \quad (10)$$

where \bar{V}°_I and \bar{V}°_{II} are the molal volumes of water in each state. Since we can neglect the compression effect¹⁾ for such weakly hydrated (bulky monovalent) ions as R_4N^+ and ClO_4^- ,

$$\text{sign of } \left(\frac{\partial \tau_e}{\partial P} \right) = \text{sign of } \left(\frac{\partial h}{\partial P} \right). \quad (11)$$

From Eqs. (7) and (10), we have

$$\text{sign of } \left(\frac{\partial W}{\partial P} \right) = \text{sign of } (\bar{V}^{\circ}_{II} - \bar{V}^{\circ}_I), \quad (12)$$

if $h > 0$.

Eq. (12) means that the density of the hydration shell is larger than that of the bulk water if the Walden product of the ion has a negative pressure coefficient and *vice versa*. As shown in Fig. 2, $\partial W(ClO_4^-)/\partial P$ is strongly negative at 1 atm and comes to be nearly zero at about 5,000 atm. Therefore, we could say the density of the water molecules in the vicinity of ClO_4^- ion is higher than that of the bulk water at the lower pressures and the difference becomes very small at about 5,000 atm. This higher density around ClO_4^- ion could be accounted for by its breaking effect on the water structure which would become weaker at high pressures because pressure would break down the water structure. Furthermore, concerning the two types of molecular models^{33,34)} proposed for the orientation of a water molecule with respect to an anion, Buckingham's one that seems to result in the higher density of the hydration shell would be preferred especially for ClO_4^- ion. Judging from Fig. 2 and Table 6, on the other hand, the hydration shells of the tetraalkylammonium ions have slightly higher densities than that of the bulk water; $\partial W(Bu_4N^+)/\partial P$ really becomes slightly negative, if the directly measured transference number data²⁶⁾ are used for the estimation of the limiting equivalent conductances of the ions at high pressures instead of the postulate, $\lambda^{\circ(I)}(Bu_4N^+) \cdot \gamma^{\circ(I)} = \lambda^{\circ(P)}(Bu_4N^+) \cdot \gamma^{\circ(P)}$. Although it is not sufficiently known in terms of both energy and density what kind of structure of water is formed about alkyl chains, the above conclusion drawn from the pressure effect on the Walden products of Me_4N^+ , Et_4N^+ and Bu_4N^+ ions seems to be conformed with the following volumetric results: the negative contribution³⁵⁾ to the partial molal volumes of the hydrophobic hydration

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of the tetraalkylammonium ions and the depressing effect³⁶⁾ of the tetraalkylammonium ions on the temperature of maximum density of water.

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